* NOTICES *

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to the water-soluble wrapping which consists of the polyvinyl alcohol system film and this film of the chilled water fast-melting mold which improved stickiness by moisture absorption in detail about a chilled water fast-melting mold water soluble film and water-soluble wrapping.
[0002]
[Description of the Prior Art]The package of a water soluble film, a detergent, etc., etc. are broadly used as wrapping which presents water solubility from polyvinyl alcohol (henceforth [PVA]) being able to carry out [film]-izing comparatively easily, and excelling before also in intensity.
[0003]As PVA used for these, the 80 to 90% saponification thing which presents dissolved water in fuel, especially low-temperature-hot-water solubility (low-temperature fusibility) is common.
[0004]
[Problem(s) to be Solved by the Invention]However, in the conventional PVA film, even if it is using PVA of the above-mentioned partial saponification thing as the raw material, the performance satisfied not necessarily is not obtained in the use which the solubility in low temperature may be insufficient for, therefore is asked for fastmelt [in low temperature].
[0005]Since a saponification reaction advanced by the problem that film breakage of a crack etc. occurs under low temperature and low humidity, and contact with an alkaline substance, chilled water solubility fell further and there was a problem that it could not be used in a package of an alkaline substance.
[0006]On the other hand, the applicant has proposed previously the water soluble film using the denaturation polyvinyl alcohol (henceforth "the denaturation PVA") which introduced the

anionic group into PVA (Japanese Patent Application No. No. 179064 [seven to]), This is dramatically excellent in chilled water fastmelt, and can also prevent deterioration by alkali, and the film breakage under low temperature and low humidity.However, since stickiness resulting from the hygroscopicity of a film will become large if the denaturation rate is raised in order to improve chilled water fastmelt, there is a problem that humidity must be controlled, in the film of this denaturation PVA, and manufacture of wrapping.

[0007]The purpose of this invention is excellent in the PVA system water soluble film which solved the above-mentioned problem, i.e., cold melting nature, And to temperature and humidity, a change in physical properties is small, and there is no deterioration also in a package of an alkaline substance, and the stickiness accompanying moisture absorption is suppressed to the minimum, and it is in providing the PVA system water soluble film which holds the intensity as wrapping.

[0008]

[Means for Solving the Problem]The denaturation PVA whose denaturation rate according [a result of wholeheartedly examination] to an anionic group in view of the above-mentioned [this invention persons] problem is 2.0-40.0-mol %, A film on which mean particle diameter contains insoluble in water or poorly soluble impalpable powder of 150 micrometers or less, fastmelt [to chilled water which exceeds the water-soluble conventional PVA film], [have and] Even if change of physical properties is small and it not only solves problems, such as film breakage under low temperature and low humidity, and insolubilization by alkali, but absorbs moisture to temperature and humidity, it is not sticky, and it finds out that good aesthetic property is maintained, and came to complete this invention.

[0009]That is, denaturation polyvinyl alcohol and (B) mean particle diameter whose denaturation rates according [a water soluble film of claim 1] to (A) anionic group are 2.0 - 40.0-mol % contain insoluble in water or poorly soluble impalpable powder of 150 micrometers or less.

[0010]A thing of claim 2 is denaturation polyvinyl alcohol produced by said denaturation polyvinyl alcohol hydrolyzing into polyvinyl alcohol selectively or thoroughly after carrying out Michael addition of the vinyl compound in a water soluble film of claim 1.

[0011]A thing of claim 3 is denaturation polyvinyl alcohol produced by said denaturation polyvinyl alcohol hydrolyzing into polyvinyl alcohol selectively or thoroughly after carrying out Michael addition of acrylonitrile or the acrylamide in a water soluble film of claim 1.

[0012]Water-soluble wrapping of claim 4 becomes any 1 paragraph of claims 1-3 from a water soluble film of a statement.

[0013]

[Embodiment of the Invention]The denaturation PVA which has an anionic group which is the (A) ingredient which constitutes the water soluble film of this invention first is explained in full

detail below.

[0014](A) Although a carboxyl group, a sulfone group, a phosphate group, etc. are mentioned as a kind of anionic group of the denaturation PVA of an ingredient, a carboxyl group and a sulfone group are desirable in respect of economical efficiency and the ease of carrying out of manufacture.

[0015]As the carboxyl group denaturation PVA used for this invention, For example, what is called the copolymerization denaturation PVA acquired by saponifying after carrying out copolymerization of vinyl acetate, itaconic acid, or the maleic acid, what is called the post-denaturation PVA acquired by introducing a carboxyl group into PVA directly, etc. are mentioned.

[0016]As a method of introducing a carboxyl group into PVA by post-denaturation, The method of carrying out piece esterification of the PVA by a maleic anhydride etc., a method to which PVA is made to carry out the substitution reaction of the monochloroacetic acid etc., There are a method to which PVA is made to carry out the Michael addition reaction of the acrylic acid etc., the method of making it hydrolyze selectively or thoroughly, after carrying out the Michael addition reaction of acrylonitrile, the acrylamide, etc. similarly, etc. Among these, conversion is high and the method of hydrolyzing in that the thing of a high denaturation rate is obtained, after carrying out Michael addition of acrylonitrile or the acrylamide is desirable.

[0017]On the other hand as a method of introducing a sulfone group into PVA, For example, vinyl acetate, vinylsulfonic acid, styrene sulfonic acid, allylsulfonic acid, There are a method of making PVA carry out Michael addition of the method of saponifying, after carrying out copolymerization of meta-allylsulfonic acid, the 2-acrylamido-2-methyl propane sulfonic acid (henceforth AMPS), etc., vinylsulfonic acid or its salt, AMPS, or its salt, etc. Among these, conversion is high and the method of making PVA carry out Michael addition of AMPS or its salt in that the thing of high denaturation is obtained is desirable.

[0018]Na salt, K salt, etc. are mentioned as a salt of above-mentioned AMPS.

[0019]The above-mentioned anion-ized agent and two or more sorts of degeneration methods may be used [in / with a natural thing / manufacture of the anion denaturation PVA] together.

[0020]2.0-40.0-mol% of the denaturation rate by an anionic group is desirable, and is more desirable. [4.0-30-mol% of] While fastmelt [to chilled water] falls that it is less than [2.0 mol %], there is a possibility of causing the film breakage under low temperature and low humidity. The thing exceeding 40.0-mol % on the other hand is difficult to manufacture.

[0021]Although the degree of polymerization in particular of the above-mentioned anion denaturation PVA used by this invention is not limited, 200-8,000 are preferred and 300-4,000 are more preferred. Sufficient film strength is not obtained with a degree of polymerization being less than 200. On the other hand, since not only fastmelt [to chilled water] falls, but aqueous solution viscosity will become high if a degree of polymerization exceeds 8,000, it

cannot dissolve in high concentration but the problem that productivity falls arises.

[0022]Next, the insoluble in water or poorly soluble impalpable powder of the (B) ingredient is explained in full detail.

[0023]The mean particle diameter of the insoluble in water or poorly soluble impalpable powder used for this invention is 150 micrometers or less, and is 50 micrometers or less preferably.

[0024]If mean particle diameter exceeds 150 micrometers, the addition taken to prevent stickiness of a film will increase, as a result, aesthetic property will be spoiled, and film strength will also fall.

[0025]As a kind of insoluble in water or poorly soluble impalpable powder used for this invention, Clay, kaolin, aluminium hydroxide, calcium carbonate, a titanium dioxide, barium sulfate, a satin white, talc, a silicate, pulp, cellulose, etc. are mentioned, and using independently if needed can also use together two or more sorts of these.

[0026]Although all of such impalpable powder prevent the stickiness accompanying moisture absorption and the influence on film properties is suppressed to the minimum, pulp, cellulose, calcium carbonate, clay, and kaolin are excellent in especially this point.

[0027]As an addition of these impalpable powder, 0.5 to 40 % of the weight is preferred to the denaturation PVA of the (A) ingredient, and 2.0 to 20% is more preferred. The stickiness prevention accompanying the moisture absorption which is an effect of this invention as it is less than 0.5 % of the weight is not enough. On the other hand, if it exceeds 40 % of the weight, it will become difficult to acquire the film properties for which it was suitable as wrapping.

[0028]Thus, on the occasion of film-izing of the obtained denaturation PVA system constituent, a process in particular is not restricted but can apply correspondingly the process of a publicly known PVA film conventionally.

[0029]For example, after preparing the solution (impalpable powder is carrying out suspension distribution) of these denaturation PVA system constituent, the cast is carried out to plastic films, such as PET, a release paper, a belt, or drum lifting, and the casting method to dry is common.

[0030]Although the thickness of the film of this invention can be arbitrarily set up according to the purpose of use, as for the thickness of the film eventually obtained also in which film-ized method, 10-100 micrometers is preferred in respect of mechanical strength and water fastmelt, and its 10-70 micrometers are [thickness] more preferred.

[0031]Since pliability is given, a plasticizer can be used for the film of this invention if needed. As a plasticizer used for these, the plasticizer used for the usual PVA film can be used, and ethylene glycol, glycerin, diglycerol, and a low-molecular-weight polyethylene glycol (molecular weight: 600 or less) are especially good. Colorant, a release agent, etc. can be blended or

applied within limits which do not spoil the meaning of this invention. For the purpose of the prevention from blocking, or improvement in a fine sight, irregularity working, such as embossing, may be performed to a film.

[0032]The water-soluble PVA system film of this invention produced by performing it above is a raw material with which has fastmelt [excellent in chilled water], do not deteriorate in the package of an alkaline substance etc., and also it has a raw material and the intensity as wrapping. Therefore, it has the performance which was dramatically excellent as wrapping, such as agricultural chemicals.

[0033]The chilled water fastmelt as used in the field of this invention means the high-speed solubility of the film shown in the water temperature of 10 ** or less. Although the film of this invention is suitably used as the water transfer film which is a use of the water soluble film currently used conventionally, or various unit wrapping, it can also be used as wrapping which had restriction in use in the further conventional water soluble film and which requires fastmelt [in low water temperature].

[0034]

[Example]Hereafter, an example explains this invention still in detail. Among a sentence, as long as there is no notice especially about a part or %, and a certain thing, it is a weight reference.

[0035]1.(A) 75 copies of example of manufacture manufacture 1 vinyl acetate of an ingredient, 500 copies of methanol, 4.85 copies of itaconic acid, 1.10 copies of NaOH(s), and 0.3 copy of azobisisobutyronitrile were taught to the separable flask, and it polymerized at 70 ** for 9 hours. The conversion at this time was 81%. After removing unreacted vinyl acetate, 1/10 of the amount of theories of NaOH(s) were added, and it saponified at 40 ** for 5 hours. The degree of polymerization of the acquired carboxyl denaturation PVA was 1,200, and the saponification degree was 96.3-mol %. When analyzed by NMR, the carboxyl denaturation rate was 3.3-mol %.

[0036]490 copies of PVA(s) (degree-of-polymerization 500 and saponification degree % of 88.2 mol), 200 copies of 30%-NaOH(s), 420 copies of 50%-aqueous acrylamide solutions, and 200 copies of isopropyl alcohol were added to the horizontal spindle blender of example of manufacture 24 liter capacity, and it stirred at 60 ** for 8 hours. Subsequently, 50 copies of 50%-NaOH(s) were added and hydrolysis was performed at 70 ** for 1 hour. It dried, after methanol refined the obtained powder, and white powder was obtained. When this thing was analyzed by NMR, the 12.2-mol % and amide denaturation rate of the carboxyl denaturation rate was 8.9-mol %.

[0037]440 copies of PVA(s) (degree-of-polymerization 2,500 and saponification degree % of 98.8 mol), 200 copies of 30%-NaOH aqueous solutions, and 484 copies of 50%-aqueous acrylamide solutions were added to the horizontal spindle blender of example of manufacture

34 liter capacity, and it stirred at 60 ** for 8 hours. Subsequently, 100 copies of 50%-NaOH(s) were added and hydrolysis was performed at 90 ** for 1 hour. When the obtained powder was analyzed by NMR, the carboxyl denaturation rate was 29.3-mol %.

[0038]Instead of 484 copies of 450% of example of manufacture-aqueous acrylamide solutions, the same operation as the example 3 of manufacture was performed except [all] having used 250 copies of acrylonitrile. When the obtained powder was analyzed by NMR, the carboxyl denaturation rate was 37.6-mol %.

[0039]440 copies of PVA(s) (degree-of-polymerization 1,700 and saponification degree % of 98.5 mol), 280 copies of 50%-NaOH aqueous solutions, and 828 copies of 50%-AMPS solution were added to the horizontal spindle blender of example of manufacture 54 liter capacity, and it stirred at 80 ** for 7 hours. When the obtained powder was analyzed by NMR, the sulfone group denaturation rate was 14.3-mol %.

[0040]440 copies of PVA(s) (degree-of-polymerization 5,000 and saponification degree % of 98.2 mol), 70 copies of 30%-NaOH aqueous solutions, and 284 copies of 50%-aqueous acrylamide solutions were added to the horizontal spindle blender of example of manufacture 64 liter capacity, and it stirred at 60 ** for 4 hours. Subsequently, 125 copies of 50%-NaOH(s) were added and hydrolysis was performed at 70 ** for 1 hour.

[0041]Subsequently, 460 copies of 50%-AMPS sodium salt solution was added, and it stirred at 80 ** for 4 hours. When the obtained powder was analyzed by NMR, the 17.3-mol % and sulfone group denaturation rate of the carboxyl denaturation rate was 6.5-mol %.

[0042]2. Impalpable powder ((B) ingredient) was blended with native [for the denaturation PVA ((A) ingredient) of the preparation examples 1-6 of a film, the comparative example 1, and the examples 1-6 of manufacture acquired by the 2 above, and comparison / PVA] at a rate shown in Table 1, and eight sorts of films for an examination were prepared by the following method.

[0043]

[Table 1]

	変性ＰＶＡの種類	（Ｂ） 成 分		
		種 類	平均粒径	添加量[1]
実施例 1	製造例１の変性ＰＶＡ	パルプ	２１	5
実施例 2	製造例２の変性ＰＶＡ	カオリン	４３	１０
実施例 3	製造例３の変性ＰＶＡ	炭酸カルシウム	3	１０
実施例 4	製造例４の変性ＰＶＡ	炭酸カルシウム	１０	３５
実施例 5	製造例５の変性ＰＶＡ	クレー	１３	２０
実施例 6	製造例６の変性ＰＶＡ	セルロース	7	１５
比較例 1	製造例５の変性ＰＶＡ	－	－	－
比較例 2	未変性ＰＶＡ[2]	炭酸カルシウム	3	１０

1) 対変性ＰＶＡ重量％
2) 重合度1700，けん化度 88.2 モル％

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[0044][Preparation of a film] First, after making water carry out suspension distribution of the impalpable powder of the (B) ingredient, to the sum (a part for however, solid) of the denaturation PVA of the (A) ingredient, and the weight of these (A) (B) both ingredients, 3% of glycerin was added and it dissolved. The solution viscosity at this time was adjusted so that it might become 15000 - 25000 mPa-s (BH type viscosity meter, 20 rpm, 25 **). Subsequently, these were cast on the PET film, it dried at 100 ** after 24-hour neglect for 1 hour, and the 40-micrometer-thick film for an examination was prepared.

[0045]3. About the evaluation profitable **** film of the film, system performance testing was carried out by the following method. The result was indicated to Table 2.

[0046][Dissolution rate to water] The examination film was cut to 1 cm x 1 cm, and the seal of + was put by aquosity magic. 500 cc of 10 ** water was beforehand prepared for a 1-l. beaker, said film was dropped all over the stillness water surface, and time until the seal of + disappears thoroughly was measured. When a film adhered to the round relaxation and beaker side, it measured again. The result displayed 3 times of average value in the "second." Even the water temperature of 5 ** was evaluated completely like the above.

[0047][Mechanical strength] The examination film was held under the condition of 20 ** and 65%RH for 72 hours, and tensile strength (TB:kg/cm^2) and a pace of expansion (EB:%) were measured according to JIS K7127, and tearing strength (TR:kg/cm) was measured according to JIS K7128.

[0048][Alkali resistance test] The examination film was cut to 1 cm x 1 cm, and it put on the petri dish, and Na_2CO_3 was carried on the film, the film concerned was covered by Na_2CO_3, and the dissolution rate to the water above-mentioned after one-month neglect in 40 ** oven was measured. What is not dissolved in 300 seconds presupposed that it is insoluble.

[0049][Tactile feeling (aesthetic property)] Tactile feeling after neglecting a film under 25 ** and

RH80% of conditions for 5 hours was judged in accordance with the following standards by a feel.

[0050]O :good ** : the x:stickiness which is sticky for a while bent the film neglected under large [film breakage] 0 ** and RH20% of conditions for 48 hours, and evaluated the existence of the film crack.

[0051][Overall evaluation] The above-mentioned system-performance-testing result was judged synthetically, and it evaluated in five steps.

[0052](It is good) 5->4->3->2->1 (bad)

[Table 2]

		水溶解速度／秒		機械強度			耐アルカリ試験／10℃（秒）	触感	フィルム破損	総合評価
		10℃	5℃	TB(kg/cm²)	EB(%)	TR(kg/cm)				
実施例	1	40	59	339	100	34	45	○	無	4
	2	33	45	365	100	39	33	○	無	5
	3	25	33	346	100	39	24	○	無	5
	4	22	35	395	95	43	22	○	無	5
	5	15	23	290	140	27	12	○	無	4
	6	48	64	345	120	35	59	○	無	4
比較例	1	17	24	310	100	25	22	×	無	3
	2	140	110	390	90	46	不溶	○	有	1

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[0053]

[Effect of the Invention]The anion denaturation PVA and mean particle diameter which have the outstanding chilled water fastmelt, alkali resistance, etc. contain insoluble in water or poorly soluble impalpable powder of 150 micrometers or less, and the PVA system film of this invention possesses the performance outstanding as a water soluble film.

[0054]That is, the water soluble film of this invention according to claim 1 to 3 is stable to 3. temperature and humidity which does not deteriorate easily even if it contacts medicine, such as 2. alkali which dissolves promptly also to 1. chilled water, and there are few changes in physical properties. For example, even if it absorbs moisture under excellent in mechanical strength as 4. film and wrapping which can prevent the film crack under low temperature and low humidity (0 **, 20%), etc. 5. high humidity, it is not sticky, and it has the features -- good tactile feeling is maintained.

[0055]Therefore, the water-soluble wrapping of claim 4 which consists of a water soluble film of this invention, When each above-mentioned feature is provided, for example, it uses for agricultural-chemicals wrapping etc., while being able to prevent plugging of the nozzle of a spray pump, the quality degradation in [according to / medicine] environment with inferior

temperature and humidity conditions can be controlled.

[Translation done.]